Low platinum loading PtNPs/graphene composite catalyst with high electrocatalytic activity for dye-sensitized solar cells*

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Platinum nanoparticles (PtNPs)/graphene composite materials are synthesized by a controlled chemical reduction of H_2PtCl_6 on graphene sheets. The electrocatalytic activity of a PtNPs/graphene composite counter electrode for a dye-sensitized solar cell (DSSC) is investigated. The results demonstrate that the PtNPs/graphene composite has high electrocatalytic activity for the dye-sensitized solar cell. The cell employing PtNPs (1.6 wt%)/graphene counter electrode reaches an conversion efficiency (η) of 3.89% upon the excitation of 100 mW/cm^2 AM 1.5 white light, which is comparable to that of the cell with a Pt-film counter electrode ($\eta = 3.76\%$). It suggests that one can use only 14% Pt content of the conventional Pt-film counter electrode to obtain a comparable conversion efficiency. It may be possible to obtain a high performance DSSC using the PtNPs/graphene composite with a very low Pt content as a counter electrode due to its simplicity, low cost, and large scalability.

Keywords: graphene, Pt nanoparticles, counter electrode, dye-sensitized solar cells

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1. Introduction

In recent years, dye-sensitized solar cells (DSSCs) have received much attention as a new type of solar cell due to their potential low cost and respectable energy conversion efficiency.[1−4] The counter electrode is an indispensable component in a DSSC, which catalyzes the reduction of triiodide (I_3^-) to iodide (I^-) after electron injection.[5] As the most commonly used catalytic material, the platinum (Pt) film counter electrode has a high catalytic activity. However platinum is an extremely expensive metal, and a Pt film is generally prepared by sputtering which not only increases the cost but also limits the maximal size of the film and its large-scale preparation. Recently, the reports show that Pt nanoparticles/graphene composite materials combine the attractive electrocatalytic behaviour of graphene with the good electronic[6,7] and catalytic properties of Pt nanoparticles (PtNPs),[8−10] and have potential applications as DSSCs counter electrodes.[11−13]

In this study, we use a very simple and low cost method to fabricate the PtNPs/graphene composite materials. It is based on a controlled chemical reduction of H_2PtCl_6 on the graphene sheets, which has not been used to fabricate counter electrodes for DSSCs yet. The results show that the conversion efficiency of a PtNPs/graphene-based DSSC with 1.6 wt% PtNPs loading is comparable to that of a Pt-film-based DSSC. The weight of Pt in a counter electrode with PtNPs (1.6 wt%)/graphene composite is only 14% of that in a conventional counter electrode with 100-nm Pt film, which means that one can save 86% noble Pt by using the composite catalyst presented here. Due to its simplicity, low cost, and large scalability, there is potential for the use of the PtNPs/graphene composite as a counter electrode to obtain a high-performance DSSC.

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2. Experimental details

2.1. Preparation of Pt/graphene composite

Graphene sheets were prepared in two steps: graphite powder (from the Qingdao Black Dragon Graphite Co., Ltd, China) was oxidized to graphite oxide (GO) via a modified Hummers method,[14] then it was exfoliated and reduced by treating the GO power in a microwave oven at 800 w for 2 min to obtain graphene sheets.

The PtNPs formed on graphene sheets were prepared according to a reported procedure. A 100-mg graphene sample was pre-dispersed in 5-mL dimethylformamide (DMF), and then mixed with 0.25-M NaOH in a 50-mL ethylene glycol solution. H_2PtCl_6 solution (10 mM) was added and ultrasonically stirred for 1 h. The Pt/graphene weight ratio was controlled by the volume of the H_2PtCl_6 solution. The solution was then stirred at 160 °C for 3 h in an oil bath. The solution was filtered and washed with distilled water and ethanol three times. The filtered cake was dried in air and then sintered at 250 °C for 1 h to remove organic compounds. Finally, a mixture powder of PtNPs/graphene was obtained.

2.2. Preparation of counter electrode

The 100-nm-Pt-film counter electrode, prepared by sputtering, was purchased from Heptachroma Solar Tech (Dalian, China). The effective area is 5×5 mm^2.

To obtain the PtNPs/graphene paste, 100-mg PtNPs/graphene composite was ground in a mortar with 30 mg hydroxyethyl cellulose and a mixed solution with 2-ml distilled water and 2-ml ethanol. The PtNPs/graphene counter electrode was prepared by coating the paste on fluorine-doped tin oxide (FTO) conductive glass using the doctor-blading technique. The counter electrode was heated in air at 180 °C for 2 h and then dried in a vacuum oven at 120 °C for 10 h. The weight of the PtNPs/graphene and hydroxyethyl cellulose on the FTO is 0.60 mg. The weight of the PtNPs/graphene is therefore about 0.46 mg

2.3. Materials characterization

The crystal structure of samples was investigated by X-ray powder diffraction (XRD) on an X-ray diffractometer (DX-2700, China) with Cu Ka radiation. The morphology of graphene and PtNPs/graphene composite were explored using an FEI Inspect field emission scanning electron microscope (FE-SEM) equipped with an X-ray energy dispersive spectrometer (EDS).

2.4. Electrochemical measurements

Nanocrystalline TiO_2 electrodes, platinum counter electrodes, electrolyte (DHS-E23) and N719 dye were purchased from Heptachroma Solar Tech (Dalian, China). The TiO_2 electrode (TiO_2 area 0.36 cm^2) was immersed in a 0.3 mM N719 dye/ethanol solution for 12 h to form the sensitized photoanode. The internal space between the photoanode and counter electrode was filled with electrolyte. The photocurrent-voltage (J–V) characteristics and electrochemical impedance spectra (EIS) were carried out on electrochemical workstation (CHI660C, China) upon the excitation of 100 mW/cm^{-2} AM 1.5 white light.

3. Results and discussion

3.1. Microstructure characterization of counter electrode

Figure 1 shows the XRD patterns of graphite powder, graphite oxide and graphene sheets. The XRD pattern of graphite powder exhibits a characteristic peak (002) of graphite at 26.31°. The interlayer distance obtained from the characteristic peak is 0.339 nm in graphite. The distance is markedly expanded to 0.964 nm ($2\theta = 9.17°$) with oxidation to form graphite oxide, which is ascribed to the formation of hydroxyl, epoxy, and carboxyl groups.[15] These results suggest that the graphite powder is completely oxidized to form graphite oxide. After microwave irradiation treatment, the diffraction peak of graphite oxide disappears, indicating that the graphite oxide is successfully exfoliated and reduced to graphene sheets.

As shown in Fig. 2(a), graphene sheets with a few layers exhibit a curly morphology consisting of a thin wrinkled paper-like structure, which contributes to large specific surface area. Graphene sheets each with high surface areas may be an ideal support for depositing metal nanoparticles. Indeed, as shown in Fig. 2(b), the PtNPs/graphene composite (Pt 1.6 wt%) can be successfully synthesized via a controlled chemical reduction of H_2PtCl_6, where Pt nanoparticles are dis-

tributed on the graphene sheets. Because the aggregation of Pt nanoparticles significantly reduces the electrocatalytic surface area,[16,17] it is important to avoid the aggregation of Pt nanoparticles in the formation of PtNPs/graphene composite catalyst. From Fig. 2(b), one can observe that Pt nanoparticles on graphene sheets do not severely aggregate, and the Pt nanoparticles with an average diameter of about 30 nm are dispersed on the graphene sheet surfaces.

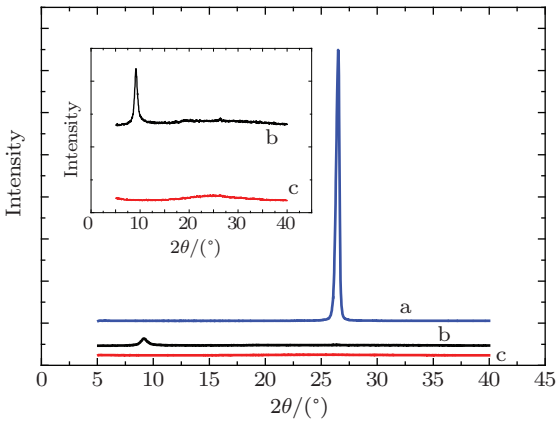


Fig. 1. (colour online) The XRD patterns of (a) graphite powder, (b) graphite oxide and (c) graphene sheets. The insert shows the magnified XRD patterns of (b) graphite oxide and (c) graphene sheets.

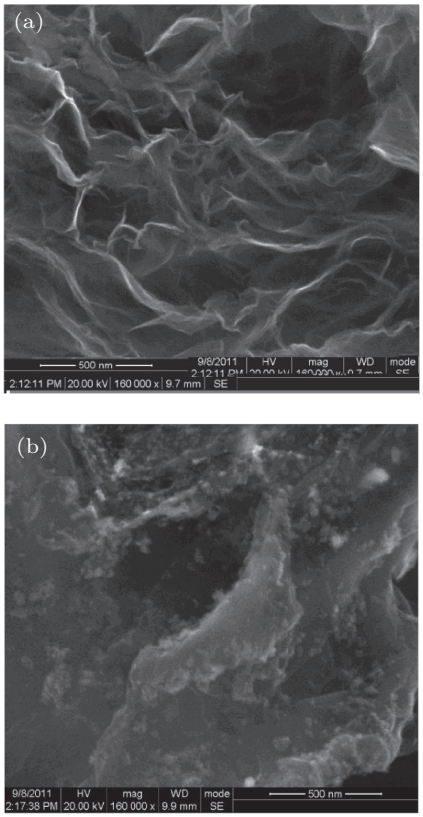


Fig. 2. The FE-SEM images of (a) graphene sheets and (b) PtNPs/graphene composite catalyst (Pt 1.6 wt%).

The EDS spectrum in Fig. 3 further confirms that Pt nanoparticles are formed on graphene sheets. Pt nanoparticles are loaded on graphene sheets via a controlled chemical reduction of H_2PtCl_6 and the content of Pt is estimated to be 1.69 wt% which is nearly consistent with the predetermined Pt/graphene weight ratio 1.6 wt%. The oxygen signal indicates that the conversion of graphene oxide to graphene is incomplete. There are also some O-containing functional groups in the graphene sheets.

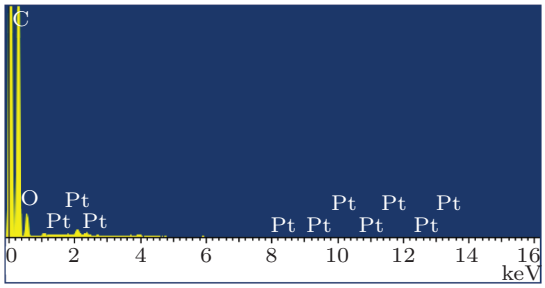


Fig. 3. (colour online) The EDS spectrum of the PtNPs/graphene composite catalyst (Pt 1.6 wt%).

3.2. Photovoltaic performance of DSSCs with a PtNPs/graphene counter electrode

Figure 4 illustrates the photocurrent-voltage curves of the cells with graphene, PtNPs/graphene (Pt 1.6 wt%) and Pt-film counter electrodes respectively. The cell employing a PtNPs/graphene (Pt 1.6 wt%) counter electrode reaches an conversion efficiency (η) of 3.89%, which is slightly larger than the value for the platinum-based cell (η = 3.76%), where the conversion efficiency is defined as the maximum power output from the cell divided by the input power from the light source. It is noticeable that the Pt areal weight in a PtNPs (1.6 wt%)/graphene composite counter electrode is $\sim 2.96 \times 10^{-4}$ mg/mm^2 (The weight of PtNPs/graphene is $\sim$ 0.46 mg, which is obtained in Subsection 2.2), and the Pt areal weight in the 100-nm-Pt-film counter electrode is $\sim 2.14 \times 10^{-3}$ mg/mm^2. This means that one can save $\sim$ 86% noble Pt metal by using the PtNPs/graphene composite catalyst. This suggests that it needs only $\sim$ 14% Pt of a conventional Pt-film counter electrode to obtain a comparable conversion efficiency by using the present simple method.

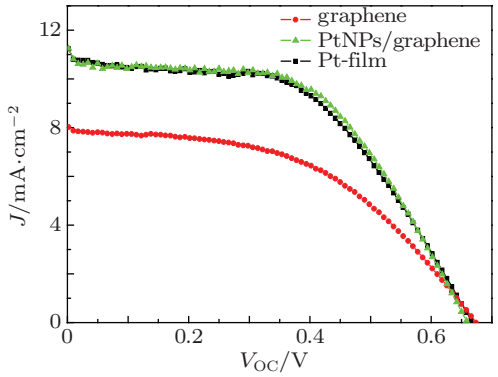


Fig. 4. (colour online) Photocurrent–voltage (J–V) characteristics of DSSCs with graphene, PtNPs/graphene (Pt 1.6 wt%) and Pt-film counter electrodes under irradiation of 100 mW/cm^2 AM 1.5 white light respectively.

Table 1 summarizes the photovoltaic performance of DSSCs based on graphene, PtNPs/graphene and Pt-film counter electrodes with different platinum loadings. When a graphene electrode without platinum is used as the counter electrode, the open-circuit voltage (V_{oc}) is 0.672 V, the short-circuit photocurrent density (J_{sc}) is 8.02 mA cm^{-2} and the efficiency (η) is 2.61%. When the platinum loading is 0.8 wt%, the open-circuit voltage is 0.640 V, the short-circuit photocurrent density is 10.97 mA/cm^{-2} and the efficiency increases to 3.71%. This is mainly due to the fact that the platinum nanoparticles loading graphene sheets form the PtNPs/graphene composite catalyst, which combines the attractive electrocatalytic behaviour of graphene with the good catalytic properties of Pt nanoparticles. It is noted that when the platinum loading is added up to 1.6 wt%, the efficiency increases to 3.89%, but when the platinum loading is added up to 2.4 wt%, the efficiency starts to decrease (3.72%). This means that the aggregation of Pt nanoparticles will increase with the increase in content of Pt in the platinum loading. Based on our results, the 1.6 wt% platinum loading on the graphene is an optimal value for catalyzing the I^-/I_3^- redox couple in the electrolyte system, and the corresponding value of efficiency is comparable to that for the Pt-film counter electrode.

Table 1. Photovoltaic performances of DSSCs based on graphene, Pt-film, and PtNPs/graphene counter electrodes with different platinum loadings.

Platinum loading/wt%	J_{sc}/mA·cm^{-2}	V_{oc}/V	FF/%	η/%
0 (graphene)	8.02	0.672	48.52	2.61
0.8	10.97	0.640	52.80	3.71
1.6	11.25	0.662	52.31	3.89
2.4	11.16	0.642	51.98	3.72
100 (Pt film)	11.23	0.672	50.70	3.76

3.3. Electrochemical measurements

To further investigate the catalytic activity of the counter electrode materials, we measure the EIS spectra of DSSCs with graphene, PtNPs/graphene (Pt 1.6 wt%) and Pt-film counter electrodes as shown in Fig. 5. The series resistance (R_s) can be obtained from the high-frequency (100 kHz) intercept on the real axis, and mainly describes the resistance of the substrate.[18] The charge-transfer resistance (R_{ct}) at the counter electrode interface can be estimated from half the value of the real semicircle on the high frequency side, which represents the catalytic activity of the electrode for reducing I_3^- ions.[19] In Fig. 5, R_s and R_{ct} for PtNPs/graphene (Pt 1.6 wt%) are calculated to be 37.38 and 4.97 Ω respectively, whereas R_s and R_{ct} for graphene counter electrodes are obtained to be 41.6 and 15.94 Ω. The lower R_{ct} value of the cell with PtNPs/graphene counter electrode is due to the higher catalytic ability of the PtNPs/graphene for the reduction of I_3^-. In the case of the Pt-film counter electrode, R_s and R_{ct} are estimated to be 33.24 and 5.04 Ω, which are close to the values of R_s and R_{ct} for Pt/graphene (Pt 1.6 wt%). It means that the PtNPs/graphene has a similar catalytic ability to the Pt-film counter electrode. The EIS results are consistent with the results of the photocurrent-voltage (J–V) characteristics of DSSCs as shown in Fig. 4 and Table 1.

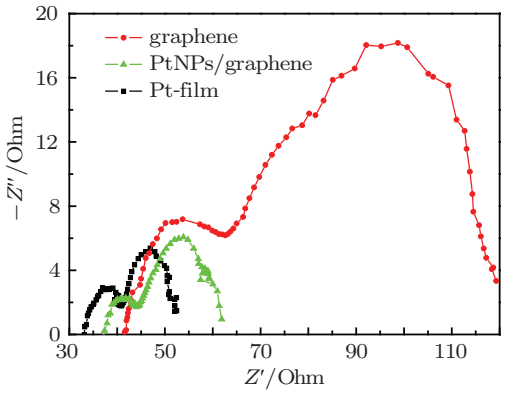


Fig. 5. (colour online) The EIS spectra of DSSCs with graphene, PtNPs/graphene (Pt 1.6 wt%) and Pt-film counter electrodes.

4. Conclusions

Pt nanoparticles are successfully synthesized on graphene sheets by reducing H_2PtCl_6. The PtNPs/graphene composite catalyst has a high electrocatalytic activity for a dye-sensitized solar cell. Compared with the conventional Pt-film (100 nm) counter

electrode, the PtNPs/graphene composite electrode has a comparable efficiency value while the Pt content in weight percentage is as low as 14%. Due to its simplicity, low cost, and large scalability, the use of PtNPs/graphene composites as counter electrodes shows potential for high performance DSSCs.

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